WO/2003/004591) METHOD FOR TRANSESTERIFICATION OF FATS AND/OR OILS BY MEANS OF ALCOHOLYSIS

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Applicants: PETER, Siegfried [DE/DE]; Lindenweg 3, 91080 Uttenreuth (DE).
WEIDNER, Eckhard [DE/DE]; Wasserstrasse 463a, 44795 Bochum (DE) *(US Only)*.

Inventors: PETER, Siegfried; Lindenweg 3, 91080 Uttenreuth (DE).
WEIDNER, Eckhard; Wasserstrasse 463a, 44795 Bochum (DE).

Agent: BEYER, Andreas; Wuesthoff & Wuesthoff, Schweigerstrasse 2, 81541 München (DE).

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Title: (EN) METHOD FOR TRANSESTERIFICATION OF FATS AND/OR OILS BY MEANS OF ALCOHOLYSIS
(DE) VERFAHREN ZUR UMESTERUNG VON FETT UND/ODER ÖL MITTELS ALKOHOLYSE

Abstract: (EN) The invention relates to a method for obtaining fatty acid esters, from triacyl glycerides by means of alcoholysis. The invention particularly relates to a method of the transesterification of fats and/or oils by alcoholysis, in which at least one alkyl fatty acid ester is added in such an amount during the initial phase that the resulting reaction mixture is a single phase. A higher reaction rate can thus be achieved with the method thereafter.
(DE) Die Erfindung betrifft ein Verfahren zur Gewinnung von Fettsäureestern aus Triacylglyceriden mittels Alkoholyse. Insbesondere betrifft die Erfindung ein Verfahren zur Umesterung von Fett und/oder Öl durch Alkoholyse, bei welchem zur Beschleunigung des Verfahrens in der Anfangsphase mindestens ein Alkanolfettsäureester in einer solchen Menge zugegeben wird, dass das dadurch entstehende Reaktionsgemisch einphasig wird. Dadurch kann in dem Verfahren von vornherein eine hohe Reaktionsgeschwindigkeit erhalten werden.

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Method to the transesterification of fat and/or oil by means of alcoholysis the invention relates to a method to the recovery of fatty acid esters from Triacylglyceriden by means of alcoholysis. In particular the invention concerns a method to the transesterification of fat and/or oil by alcoholysis, becomes added with which the acceleration of the method in the initial phase at least a Alkanolfettsäureester in such an amount that the reaction mixture resultant thereby becomes single-phase.

Transesterification reactions actual are known. They represent a commercial significant class industrial organic reactions. With a transesterification reaction an ester becomes by exchange of the acid groups or transfered by exchange of the alkoholschen groups into another ester. If the transesterification becomes made by exchange of the alcoholic groups, one speaks of the so called alcoholysis (also Alkanolyse). With the alcoholysis the alcohol becomes and/or. the alkanols in the excess added, around an high yield at the desired ester to obtained. In newer time in connection with the generation of diesel fuel from regenerating raw materials the preparation of < RTI ID=1.1> Alkyl star, < /RTI> in particular of methyl esters, by vegetabilische oils < RTI ID=1.2> (z.< /RTI> B. Rapsöl, Sojaöl), erheblich an Aktualität gewonnen.

The transesterification is an equilibrium reaction, which becomes usually already the triggered by mixing reactants. The reaction runs however so slow that is usually required for the commercial execution of the reaction a catalyst. As catalysts serve usually strong acidic ones or strong bases.

Fats and oils consist predominant of Glyceriden (mono, Di-und triglycerides).

With the transesterification of such fats and oils the component can become glycerol by low molecular monohydric alcohols substituted. In the practice for this the frequent method becomes after Bradshaw (described in the US patents < RTI ID=1.3> 2, < /RTI> < RTI ID=1.4> 271, < /RTI> 619 and 2, 360, 844) applied. The reaction becomes conducted in an open container, which can consist of ordinary carbon steel. The fat or oil must be drying (anhydrous), clean and above all neutral, D. h. that content at free fatty acids must be more negligible small (acid value higher < as; RTI ID=1.5> 1, < /RTI> 5). Generally the monohydric alcohol in high excess becomes added the increase of the yield and the reaction rate the reaction mixture (the equivalent ratio is often higher as 1: 6).

In a work of WRIGHTs et < RTI ID=2.1> al.< /RTI> < RTI ID=2.2> (HJ. WRIGHT, J.< /RTI> B. Segur, H. V. Clark, S. K. Coburn, E. E. Langdon and R. N. DuPuis, oil & Soap, 21 [1944] 145-148) became the exact conditions for the alcoholysis of fats with methanol and ethanol in the detail investigated. Further reported becomes from the authors over experiments over the alcoholysis with other monohydric alcohols. It becomes stated that the described above alcoholysis catalyzed with alkali is complete successful only if the fat is almost free of free fatty acids and the reaction mixture free of water. If one of these conditions is not met, it comes to the saponification, which < a loss to alkalinity and the formation of one; RTI ID=2.3> Gelstruktur< /RTI> to the sequence, those has the separation and the settling of the glycerol prevented or slowed.

The transesterification of the Triacylglyceride by means of alcoholysis is characterised in that the reaction between alkanols and Triacylglyceriden of a start-up phase requires, in which only a small reaction rate exists, because the reaction component is not alkanols in the oil soluble. Particularly with the preparation of methyl esters this circumstance is very disturbing, since methanol is only little soluble in the umzuesternden oils and fats. On the other hand methanol is in the methyl esters of the fatty acids good soluble. Pathways of the small < RTI ID=2.4> Methanolkonzentration< /RTI> in the oil the transesterification reaction runs off only slow one. The reaction mixture must become vigorous mixed to finally that content at esters so far rose that the reaction mixture becomes single-phase and the reaction rate sudden strong rises.

As catalysts alkali metals or alcoholates of the alkali metals become used in the practice. The alkaline catalysts dissolve in the reaction mixture, D. h. the reaction becomes homogeneous catalyzed. The alkali metals and their alcoholates become in courses of the reaction soaps the reacted, which particularly separate in the resultant glycerol and whose subsequent treatment to pure glycerol raise the price of. In addition, in the methyl ester remain small amounts at alkali, which might not be problem-free whole with the use of the methyl esters as diesel fuel. Therefore also heterogeneous catalyzed methods became, z in newer time. B. using a metal salt of a strong basic amino acid as solid catalyst proposed (patent application DE 199 50 593 insoluble in the reaction mixture < RTI ID=2.5> Aluminium). < /RTI>

Furthermore a catalyst on basis of titanium oxides became developed, which it has the disadvantage that the reaction temperatures within the range of < RTI ID=3.1> 240 C< /RTI> lie.

On the basis of this state of the art it is to be eliminated the object of the invention this start-up phase with moderate reaction temperatures and/or. to shorten and to arrange the method thereby more effective.

The solution of this object made by a method to the transesterification of fat and/or oil by means of alcoholysis, with which the umzuesternden fat and/or oil the execution of the alcoholysis alkanols become, in particular univalent alkanols in the excess added, characterised in that the fat and/or the oil at least a Alkanolfettsäureester in such an amount added become that the reaction mixture resultant thereby becomes single-phase with reaction conditions.

Surprisingly it was now found that already a right small amount at supplied Alkanolfettsäureestern knows a this solve the problem. The addition of the Alkanolfettsäureester can take place at it forwards, after or simultaneous with the addition of the alkanols.

After the method of this invention the initial phase becomes avoided with the transesterification thereby and/or. shortened that for example becomes added for the case of the alcoholysis with methanol a part of the continuous generated methyl esters the starting product at Triacylglyceriden in such amounts that the mixture becomes single-phase from oil, methanol and methyl ester.

If the reaction mixture in a single phase is present, the effective is < RTI ID=3.2> Alkanolkonzentration< /RTI> from the outset high and the reaction run off corresponding fast. For example with one < RTI ID=3.3> 135 C< /RTI> in the initial phase of a catalyzed process heterogeneous with Zinkarginat (methyl ester production from palm oil) a Reakti< RTI ID=3.4> onsgeschwindigkeit< /RTI> from 0, < RTI ID=3.5> 8< /RTI> < RTI ID=3.6> g/Skgznarg< /RTI> and after entry of < RTI ID=3.7> Einphasigkeit< /RTI> a reaction rate of 2,5 < RTI ID=3.8> g/skgznarg< /RTI> measured.

The fat and/or oil, which in the invention process used becomes, can be in particular biological origin.

The amount < on; RTI ID=3.9> Alkanolfettsäureestern, < /RTI> to the preparation of a single-phase mixture added will must, hangs of the quality of the oil, which height < RTI ID=4.1> Alkanolüberschusses< /RTI> and the reaction temperature off. The Alkanolüberschuss becomes the increase of the reaction rate and the yield at Fettsäu< RTI ID=4.2> realkanolestern< /RTI> generally with an equivalent ratio (D. h. Ratio of mol fatty acids in the fat and/or oil to mol univalent alkanols) of 1: 6 or over it applied.

Alkanolfettsäureester, which in the method preferably added becomes, are z. B. Methyl ester, ethyl ester and/or Propylester.

< RTI ID=4.3> Alkanolfettsäureester< /RTI> preferably become in an amount from 5 to 50 Gew. - < %; RTI ID=4.4> particularly prefered 12 to 20 thread. - zugege < % related to the fat and/or oil; /RTI> user.

The invention process is particularly effective, if intended is, the transesterification in an heterogeneous catalyzed process, which preferably continuous can be to operate. In addition, with an homogeneous catalyzed method the method is favourable after this invention, because the costs for the swirl of the two phases in the initial phase of the reaction saved to become to be able. Such heterogeneous catalyzed methods become for example in the mentioned above DE 199 50 593 described.

Thus a catalyst becomes added in an other preferable embodiment the method, which can be either a soluble catalyst or in alkanols and in the reaction mixture insoluble metal salt of a amino acid or an amino acid derivative.

The solved catalyst can exist for example in solved alkali metals or Alkoholten of alkali metals.

The insoluble catalyst can exhibit a metal component, which is calcium, strontium, barium, another alkaline earth metal, or heavy metal, in particular silver, copper, zinc, manganese, iron, nickel, cobalt, lanthanum or another rare earth metal, while the amino acid component of the insoluble catalyst can contain quarternären nitrogen or a Guanidinogruppe. Particularly prefered is < the insoluble catalyst a Schwermetallsalz of the arginine, in particular the zinc salt or; RTI ID=4.5> Cadmiumsalz< /RTI> the arginine. , The catalytic active salts insoluble in the reaction mixture can be depressed thereby on a suitable carrier.

The invention process can be accomplished to particularly effective, if the portion of free fatty acids in that < umzuesterndem fat and/or oil less than 0.5; RTI ID=5.1> Gew. - < %; /RTI> in particular less than 0.1 < RTI ID=5.2> Gew. - %< /RTI> amounts to.

In addition it was found that the reaction temperatures with the heterogeneous catalyzed transesterification preferably within the range of 80 to < RTI ID=5.3> 160 C, < /RTI> in particular within the range of 100 to < RTI ID=5.4> 150 C< /RTI> to lie should.

Particularly prefered becomes in the invention process a procedure, becomes recirculated with which the Alkanolfettsäureester, which stays after separation of the glycerol from the product stream with the subsequent separation and purification of the major amount of the generated methyl esters by distillation as Sumpfprodukt. In this way simultaneous small amounts at not reacted Glyceriden become recirculated. In addition thereby one < RTI ID=5.5> Glyceringehalt< /RTI> in the final phase of the reaction reduced and the yield of the equilibrium reaction corresponding elevated. Altogether so a continuous processing becomes possible.

The amount at methyl esters, which < to the preparation of single-phaseness with reaction temperatures within the range of 100 to; RTI ID=5.6> 150 C< /RTI> prefered is, amounts to approx. 12 to 20 Gew. - %.

Subsequent one becomes the invention process at different examples near explained.

Thus the invention process at a mixture became from sunflower oil and methanol tested. In this case was sufficient with < RTI ID=5.7> 135 C< /RTI> and an equivalent ratio of mol fatty acids in the oil to methanol of 1: 6 (60 Gew. - < % sunflower oil and 40; RTI ID=5.8> Gew. - %< /RTI> Methanol) an addition of approx. < RTI

ID=5.9> 15%< /RTI> < RTI ID=5.10> Gew. - %< /RTI> Methyl ester related to the oil, in order to produce an a phase system. The adjusting pressure amounted to in the described case 5 bar. As catalyst Zinkarginat served. The Reaktionsgeschwin< RTI ID=5.11> digkeit< /RTI> amounted to < RTI ID=5.12> 2, 5 g/skgznarg.< /RTI> In this example from the beginning an high reaction rate became obtained.

In addition palm oil was < with; RTI ID=5.13> 150 C< /RTI> with methanol in the equivalent ratio of 1: 6 mixed and Zinkarginat as catalyst added. After addition of 20 < RTI ID=5.14> Gew. - %< /RTI> Methyl ester concerning palm oil was single-phase the mixture. The reaction rate was < with 3,2; RTI ID=6.1> g/skgznarg< /RTI> von vornherein hoch. The initial phase with low reaction rate was jumped over.

Palm oil was < further with; RTI ID=6.2> 85 C< /RTI> with methanol in the equivalent ratio of 1: 6 mixed and Zinkarginat as catalyst added. The reaction rate amounted to 0.05 < RTI ID=6.3> g/skgznarg.< /RTI> After by addition of methyl ester (approx. 13 < RTI ID=6.4> Gew. - %< /RTI> concerning oil) the reaction mixture was single-phase, with ambient pressure a reaction rate of 0,35 was < RTI ID=6.5> g/skgznarg< /RTI> measured.

With reaction temperatures of < RTI ID=6.6> 200< /RTI> to < RTI ID=6.7> 240 C< /RTI> become after methods with zinc soaps, described in the German patent specification DE 198 03 053 CI, as catalysts with printing up to 90 bar of triglycerides with high equivalent excess at methanol (equivalent ratio higher as 1: 6) to esters reacted. Bottom these conditions is a higher methyl ester content emergency little, in order to manufacture an a phase system, when in the example mentioned with < RTI ID=6.8> 135 C.< /RTI>

Claims < RTI ID=7.1

> 1.< /RTI> Method to the transesterification of fat and/or oil by means of alcoholysis, with which the umzuesternden fat and/or oil execution the aluminium becomes koholyse alkanols, in particular univalent alkanols in the excess added, characterised in that the fat and/or oil min destens < RTI ID=7.2> Alkanolfettsäureester< /RTI> in such an amount added becomes that the reaction mixture resultant thereby becomes single-phase.

< RTI ID=7.3> 2.< /RTI> Process according to claim 1, characterised in that the admitted < RTI ID=7.4> Alkanolfettsäureester< /RTI> selected becomes from the group, existing from ME thylestern, ethyl esters and/or Propylestern.

3. Process according to claim 1 or 2, characterised in that of the aluminium < RTI ID=7.5> kanolfettsäureester< /RTI> in an amount from 5 to 50 < RTI ID=7.6> Gew. - < %; /RTI> preferably 12 to 20 < RTI ID=7.7> Gew. - %< /RTI> related to the fat and/or oil added becomes.

4. Process according to one of claims 1 to 3, characterised in that for the execution of the reaction in the reaction mixture of soluble Ka < RTI ID=7.8> talysator< /RTI> added becomes.

5. Process according to one of claims 1 < RTI ID=7.9> to 3, < /RTI> characterised in that for the execution of the reaction the reaction mixture in Alkano len and in the reaction mixture insoluble metal salt of a amino acid or an amino acid derivative an added become.

6. Process according to claim 4, characterised in that the alcoholysis by solved alkali metals or alcoholates of the alkali metals catalyzed becomes.

7. Process according to claim 5, characterised in that < RTI ID=7.10> Metallkom < /RTI> ponente the catalyst calcium, strontium, barium, another earth alkene limetall or an heavy metal, in particular silver, copper, zinc, manganese,
Iron, nickel, cobalt, lanthanum or another rare earth metal are.

8. Process according to one of claims 5 or 7, characterised in that the amino acid component of the catalyst quarternären nitrogen or a Guanidinogruppe contains.

9. Process according to one of claims 5 or 7, characterised in that the catalyst a Schwermetallsalz of the arginine, in particular that
Zinc salt or < RTI ID=8.1> Cadmiumsalz< /RTI> the arginine is.

10. Process according to one of claims 1 to 9, characterised in that the portion of free fatty acids in that umzuesterndem fat and/or oil < RTI ID=8.2> less than 0.5 thread. - %, in particular less than 0.1 thread. - beträgt.< %; /RTI>

< RTI ID=8.3> 11.< /RTI> Process according to one of claims 1 to < RTI ID=8.4> 10, < /RTI> characterised in that the transesterification with temperatures in the range from 80 to < RTI ID=8.5> 160 C, < /RTI> preferably in the range from 100 to 150 C conducted becomes.

12. Process according to one of claims 1 to 11, characterised in that that the reaction mixture added < RTI ID=8.6> Alkanolfettsäureester< /RTI> from the product stream into the method, resultant with the transesterification, rezirku one liert.

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